Magnetoresponsive Photonic Microspheres with Structural Color Gradient

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Professor Shin passed away unexpectedly on September 30th 2016. We dedicate this work as a memorial to him.

Janus particles are composed of two or more compartments that have distinct chemical or physical properties.[1–3] Anisotropy arising from the biphasic structure provides unique material functionalities that are otherwise difficult to achieve with single-compartment particles, opening up new opportunities in various application areas.[4–7] For example, Janus particles exhibit advanced function and performance over single-compartment particles for uses as biosensors,[8] optical probes,[9] interface stabilizers,[10–14] and dual-drug carriers.[15–17] In particular, bicolored Janus particles are designed to have electric or magnetic anisotropy to serve as active color pigments for reflection-mode displays.[18,19] The orientation of such Janus particles can be exquisitely manipulated with an external field, enabling color switching; such twisting ball-type displays known as Gyricon displays.[18] The bicolored Janus particles are typically produced by emulsifying two parallel streams of distinct polymer melts or resins using either a spinning disk[18] or a microfluidic device.[19,20] The bicolored Janus particles can also be produced by using phase separation of immiscible polymers or separation induced by a magnetic field in emulsion templates.[21,22] Different compositions of chemical or colloidal pigments in the streams yield electric or magnetic anisotropy as well as optical anisotropy in the resulting Janus particles.

Recently, colloidal arrays have been employed to develop structural colors in Janus particles, instead of pigments or dyes.[23–27] The structural colors never fade as long as the structures persist and show high color purity,[28–32] thereby potentially providing enhanced color quality of displays. To produce a regular colloidal array in Janus particles, two resins containing repulsive colloids with different sizes are coemulsified and photocured. The repulsive colloids form regular lattices in each compartment, possibly yielding two different structural colors in single Janus particles.[29] Alternatively, a photocurable resin and an aqueous dispersion of colloids are coemulsified in the third oil phase, where the resin phase is photocured and the aqueous phase is dried to form colloidal crystals.[30–32] However, all the methods employ delicate microfluidic processes for the formation of two parallel biphasic flows and their coemulsification. Furthermore, emulsion drops are unstable against coalescence, thereby achieving low stability of production. In addition, defects in crystals are inevitable in the curved interfaces of emulsion drops, deteriorating optical performance.[33] More importantly, it is difficult to incorporate more than two colors due to the complexity of microfluidic channels and low stability of multiphasic emulsions; although triphasic microparticles are prepared by microfluidic technique, boundaries among phases are indistinct and the colors are dim due to mixing among the phases before photocuring.[34] This limitation requires a precise pixelation of different colored Janus particles for future uses in color displays. Therefore, it remains an important challenge to produce anisotropic particles capable of exhibiting multiple structural colors in a reproducible manner.

In this work, we report a simple but robust method to create photonic microspheres with a gradient of structural color and magnetic anisotropy, which enables the microspheres to display multiple structural colors depending on their orientation. To design the photonic nanostructure with a gradient of periodicity, we repeatedly deposit thin layers of silica and titania on the black microspheres. The high directionality of the sputtering deposition yields the 1D photonic structure, in which the thickness decreases along the curved surface of the microspheres from the north pole. Therefore, the microspheres exhibit a continuous shift of structural color along the polar angle. The microspheres can be further rendered magnetoresponsive by forming a ferromagnetic iron layer underneath the 1D photonic structure. The magnetization enables the fine control of microsphere orientation using an external magnetic field. Therefore, the structural color from the 1D photonic structure is tunable. This simple method only employs a layer-by-layer deposition technique to create a photonic structure on a microsphere, which is highly controllable and obviates defect formations. Moreover, the nature of directional deposition on a curved surface yields a gradient of periodicity in the photonic structure, providing a gradient change of structural color that is otherwise very difficult to develop in Janus microspheres.

Single-phasic microspheres dyed with black pigments are first prepared, which are then used for the layer-by-layer deposition of dielectric materials. To make the microspheres monodisperse,

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a photocurable resin of ethoxylated trimethylolpropane triacrylate (ETPTA) containing 2 wt%/wt% Sudan black B and 5 wt%/wt% photoinitiator is emulsified into 7.5 wt%/wt% aqueous solution of polyvinyl alcohol (PVA) using a capillary microfluidic device, as shown in Figure S1 (Supporting Information). The resin drops are then polymerized by in situ irradiation of ultraviolet (UV) light. The black microspheres are deposited on polystyrene (PS)-coated glass wafer, where the PS layer is 5 µm thick, to form a hexagonal array in a monolayer. To prevent movement of the microspheres during the sputtering, the microspheres are partially embedded into the underlying PS layer at 100 °C. To render the microspheres magnetoresponsive, iron is vertically deposited over the monolayer using a thermal evaporator; a condition that yields a 30 nm thick layer on a flat surface is used. The ferromagnetic iron layer, which has a large coercivity due to its thinness, as shown in Figure S2 (Supporting Information), renders the microspheres magnetoresponsive. As the direction of magnetization is set to be vertical, all the microspheres released from the wafer after deposition of dielectric layers can exhibit consistent rotational motion under an external magnetic field. Chromium is deposited over the magnetic layer before deposition of the 1D photonic structure, which increases color contrast by reducing reflection of light and improves adhesion between the iron and photonic layers; a condition that yields a 200–300 nm thick layer on a flat surface is used.[35] To create the 1D photonic structure, silica and titania are chosen as a pair of dielectric materials as their refractive index contrast is high enough to provide photonic effect with only several layers (amorphous silica has a refractive index of $n_{silica} = 1.48$ and amorphous phase titania has a refractive index of $n_{titania} = 2.53$) and a uniform layer can be easily deposited by sputtering.[36] Alternatively, the silica and titania are deposited over the chromium layer. To cover more than half of the surface of the microsphere, the directional flux of materials is applied at a deposition angle of $\alpha = 55°$ while rotating the wafer along the vertical axis. The microspheres are finally released from the wafer by partially dissolving the PS layer. The overall procedure for the production is illustrated in **Figure 1**a.

The microspheres with 1D photonic structure show pronounced color at their top surfaces. For example, microspheres with a 1D structure, composed of four pairs of silica and titania layers, show cyan (shown in Figure 1b), where the silica and titania layers are formed at the conditions by which 103 nm thick and 38 nm thick layers are formed on a flat surface, respectively. The microspheres have an average diameter of 79.6 µm and their coefficient of variation is as small as 1.88%. The reflectance spectrum from the array of microspheres has a dip at 668 nm, as shown in Figure 1c. The color at the top surface and wavelength of reflectance dip, measured from microspheres, are coincident with those of 1D photonic structure formed on flat glass wafer by the same deposition condition, as shown in Figure S3 (Supporting Information). This indicates that photonic structure on the north pole of the microsphere has the same dimensions as the flat counterpart. All the microspheres are uniformly rendered to have the same reflection color. For arbitrarily selected microspheres, no distinguishable color difference is observed, as show in Figure S4 (Supporting Information). The standard deviation in the reflectance dip position is also as small as 4.8 nm.

The microspheres in the array show additional color patterns around the center, as shown in Figure 1b and Figure S5 (Supporting Information), which are not observed when the

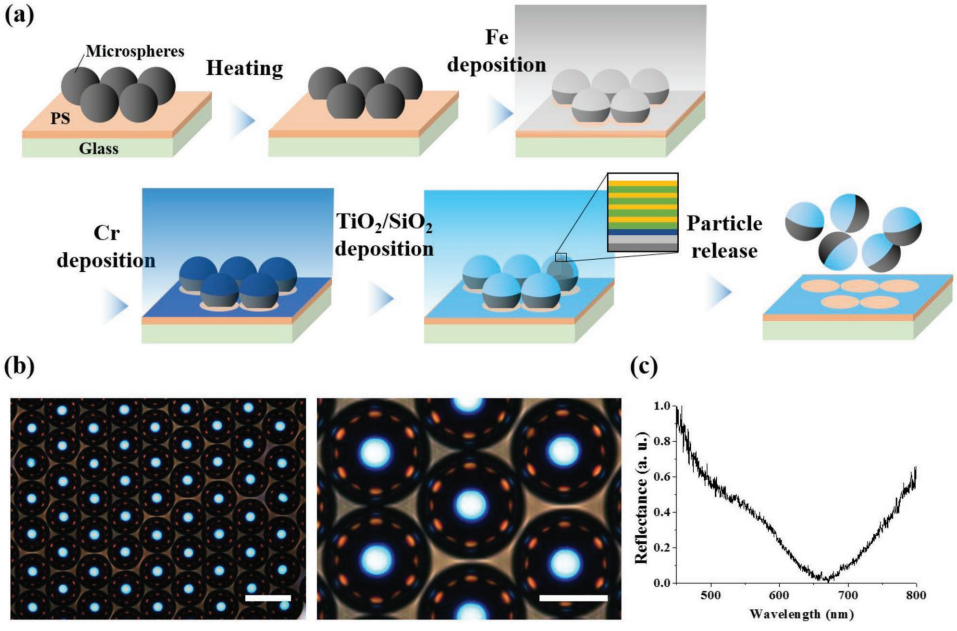

Figure 1. a) Schematic showing the fabrication procedure of photonic Janus microspheres. Black microspheres are fixed on an underlying polystyrene (PS) layer. Iron and chromium layers are deposited on the microspheres in a sequence. Silica and titania layers are then alternately deposited over the chromium layer. The microspheres are released by dissolving the PS layer. b) Optical microscopic (OM) images of photonic Janus microspheres taken at two different magnifications before release. The scale bars are 100 µm (left panel) and 50 µm (right panel). c) Reflection spectrum of the photonic Janus microspheres.

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microspheres are isolated. These color patterns are caused by multiple reflections on the surfaces of two neighboring microspheres; these have been observed in photonic drops of cholesteric liquid crystals with planar alignments and are referred to as photonic cross-communications.[37,38] Six thick and six thin red lines at a polar angle of 45° appear along the azimuthal direction in each microsphere. These red lines are caused by double reflection from two neighboring microspheres at an angle of 45°, as illustrated in Figure S5b (Supporting Information). The thick and thin lines are the results of communication with the nearest and the second nearest neighbors, respectively. Six thin blue lines appear at a polar angle of 57.5°, which is caused by triple reflection (incident light is reflected by a microsphere at an angle of 57.5°), which then impinges on the neighboring microsphere normal to the surface, thereby leading to additional reflection in the same path with an opposite direction to the incident light, as illustrated in Figure S5c (Supporting Information). The communication by the triple reflection only occurs between two nearest neighbors, thereby resulting in six lines.

The thickness of the photonic layer at the top surfaces of the microspheres is equivalent to that on a flat surface. However, the thickness decreases as the polar angle increases because material flux per surface area decreases. We roughly confirm the thickness decrease by depositing a 1.4 µm thick titania layer on the microsphere and observing the cross-section, as shown in **Figure 2**a. For the multilayer stacks of silica and titania, a gradient of structural color along the polar angle is therefore expected. We calculate the thickness variation as a function of polar angle, θ, using mass conservation with an assumption of the uniform flux of materials along the direction of deposition, as shown in Figure 2b. Details of the calculation are shown in Figure S6 (Supporting Information). The deposition with an angle of $\alpha = 55°$, while rotating the substrate, results in a higher surface coverage of 71.3% and a slower color gradient than those for the vertical deposition. Relative thickness, t/t_{max}, decreases from 1 at $\theta = 0°$ to 0 at $\theta = 145°$ for $\alpha = 55°$, whereas t/t_{max} is 0 at $\theta = 90°$ and the surface coverage is 50% for the vertical deposition with $\alpha = 0$. We confirm the color change along the polar angle by observing the microsphere on the substrate during tilting, as shown in Figure 2c,d, where the tilting angle is the same as the polar angle. As the tilting angle increases from 0° to 72°, the color is varied from cyan to magenta, green, and colorless. In addition, the dip position of reflectance spectrum is blue-shifted as the angle increases, as shown in Figure S7a (Supporting Information). This shift is consistent with that calculated from the thickness variation using a transfer matrix method with Maxwell equations, as shown in Figure 2e and Figure S7b (Supporting Information),[39] indicating the high reproducibility of the color gradient on the sphere surface. The coefficient of variation in the dip position for all angles is as small as 1%. In addition, we can verify that the red and blue

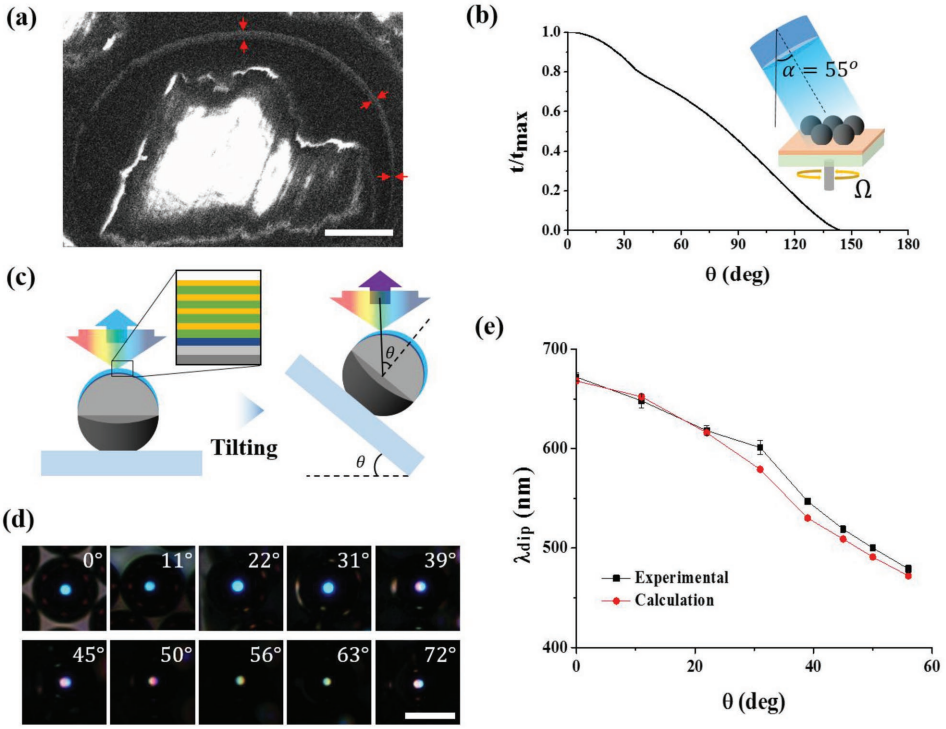

Figure 2. a) Scanning electron microscopy (SEM) image showing the microsphere cross-section. The thickness of deposited layers on the microsphere is indicated with pairs of arrows, where the thickness reduces as polar angle (θ) increases. The scale bar is 10 µm. b) Polar angle dependence of the thickness of deposited layers normalized by the maximum, t/t_{max}. Inset is a schematic of sputtering deposition for alternate photonic layers. c) Schematic showing observation of photonic Janus microsphere on a tilted substrate. d) A series of OM images showing color change as the tilting angle of the substrate, or the polar angle of the microsphere, is increased. The angle is denoted in each panel. The scale bar is 50 µm. e) Polar angle dependence of reflectance dip position, λ_{dip}. Experimental data, denoted by squares, and calculated data from thickness variation in (b), denoted by circles, are in good agreement.

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lines from cross-communication are consistent with the thickness variation. The reflectance peak for the thickness at $\theta = 45°$ and reflection angle of 45° is located at 580 nm according to Bragg's law for the second order, which is consistent with red lines from double reflection. The reflectance peak for thickness at $\theta = 57.5°$ and reflection angle of 57.5° is located at 460 nm, which is also consistent with blue lines.

Structural color can be tuned by adjusting the optical lengths of the silica and titania layers, $n_{silica}d_{silica}$ and $n_{titania}d_{titania}$, where d_{silica} and $d_{titania}$ are the thicknesses of the silica and titania layers, respectively. When the optical lengths are set to be comparable the stop band position is four times the optical length, according to Bragg's law. Therefore, to develop red color from the top surfaces of the microspheres, silica and titania layers are deposited to be 110 and 62 nm thick, respectively, as shown in **Figure 3**a. Microspheres with an average diameter of 107 µm are used. Two additional layers of silica and titania are inserted at the top and bottom, respectively, as illustrated in Figure 3d. The thicknesses of additional silica and titania layers are 55 and 31 nm, respectively, which correspond to an optical length of one-eighth of the reflectance peak wavelength. These additional layers suppress the second-order peak in the reflectance thereby enhancing color purity.[40] In the same manner to red-colored microspheres, green- and blue-colored microspheres are prepared by setting d_{silica} = 87 nm and $d_{titania}$ = 50 nm for green, and d_{silica} = 75 nm and $d_{titania}$ = 42 nm for blue, as shown in Figure 3 b,c, where additional layers are also inserted. Reflectance spectra measured from red, green, and blue microspheres are shown in Figure 3e. The reflection intensity for wavelengths longer than the stop band is reduced, as expected from two

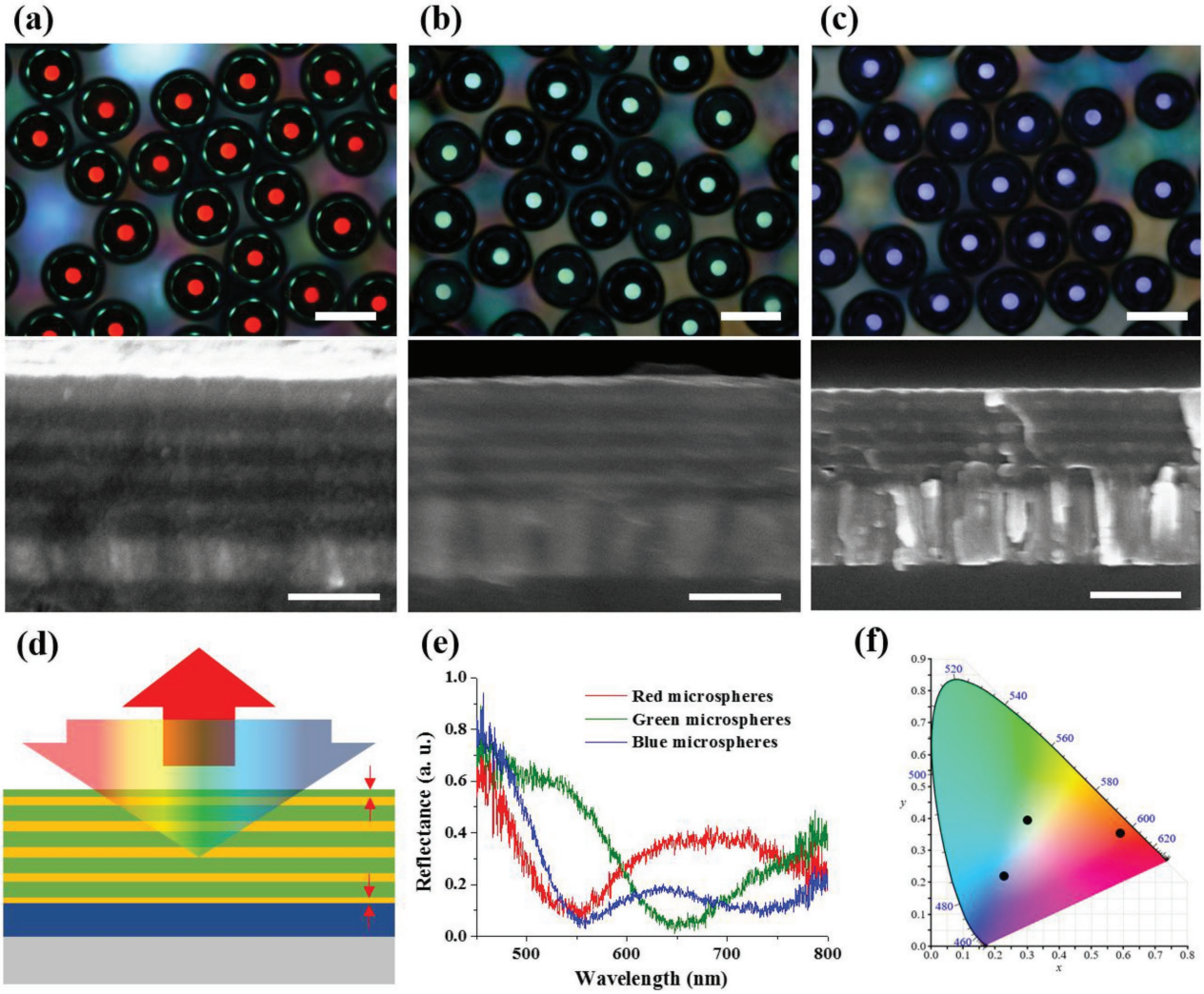

Figure 3. Sets of an OM image of photonic Janus microspheres and an SEM image showing a cross-section of photonic layers deposited on a flat surface at the same conditions as the microspheres: a) red-, b) green-, and c) blue-colored microspheres. Scale bars are 100 µm (top panels) and 500 nm (bottom panels). d) A schematic showing photonic layers on a chromium layer, where green and yellow represent silica and titania, respectively. Silica and titania layers with an optical length of $\lambda_{peak}/8$ are additionally inserted at the top and bottom of photonic layers, respectively, which are indicated by the pairs of arrows. λ_{peak} is the stop band position. e,f) Reflectance spectra and CIE chromaticity diagram of red-, green-, and blue-colored microspheres in (a–c).

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additional layers. The colors and spectra from the microspheres are comparable with those from 1D structures deposited on flat surfaces, as shown in Figure S8 (Supporting Information); the blue peak for red microspheres is attributed to reflection from the substrate. From the reflectance spectra, structural colors of red, green, and blue microspheres are plotted in Commission internationale de l'éclairage (CIE) color space, as shown in Figure 3f, which indicates how colors are seen with the naked eye.

As Janus microspheres have a gradient of structural color at one side and no structure at the other side, they can display one of the multiple colors or no color, depending on their orientation. Moreover, the microspheres are rendered to be magnetoresponsive by the iron layer. Therefore, structural color can be switched by controlling the orientation of the microspheres by manipulating the direction of the external magnetic field. To demonstrate the application of our Janus microspheres as color-switchable Gyricon pigments, we use red-colored Janus microspheres in Figure 3a. The color gradient is confirmed by observing the microsphere fixed on the substrate during the substrate tilting, as shown in Figure S9a,b (Supporting Information). The microsphere shows a pronounced red color from the top surface at $\theta = 0°$. The color blue-shifts as the angle increases: green for $\theta = 45°$ and blue for $\theta = 63°$. The polar angle dependent change of reflectance peak position, λ_{peak}, is shown in Figure S9c (Supporting Information). The experimental result is in good agreement with the calculated prediction.

Janus microspheres released from the substrate are aligned to be parallel to the direction of the external magnetic field, as shown in **Figure 4**a. Therefore, the reflection color of microspheres can be switched: red for $\theta \approx 0°$, green for $\theta \approx 45°$, blue for $\theta \approx 60°$, and no color for $\theta \approx 180°$. Continuous color change of a single microsphere during rotation is shown in Movie S1 (Supporting Information). Because all of the microspheres have the same direction of magnetization, they show collective rotational motion when the direction of the external magnetic field is changed, as shown in Movie S2 (Supporting Information). Therefore, reflection color has small microsphere-to-microsphere variation at each moment. A monolayer of Janus microspheres is used to observe the color change in a macroscopic view, as shown in Figure 4b and Movie S3 (Supporting Information). We can further confirm that the Janus microspheres can switch reflection color by selecting one in the color gradient.

In conclusion, we report a new type of photonic Janus microspheres that enables structural color switching through manipulation of an external magnetic field. The microspheres are rendered magnetoresponsive by depositing iron on the surface and optically anisotropic by alternately sputtering two different dielectric layers. High directionality and uniform

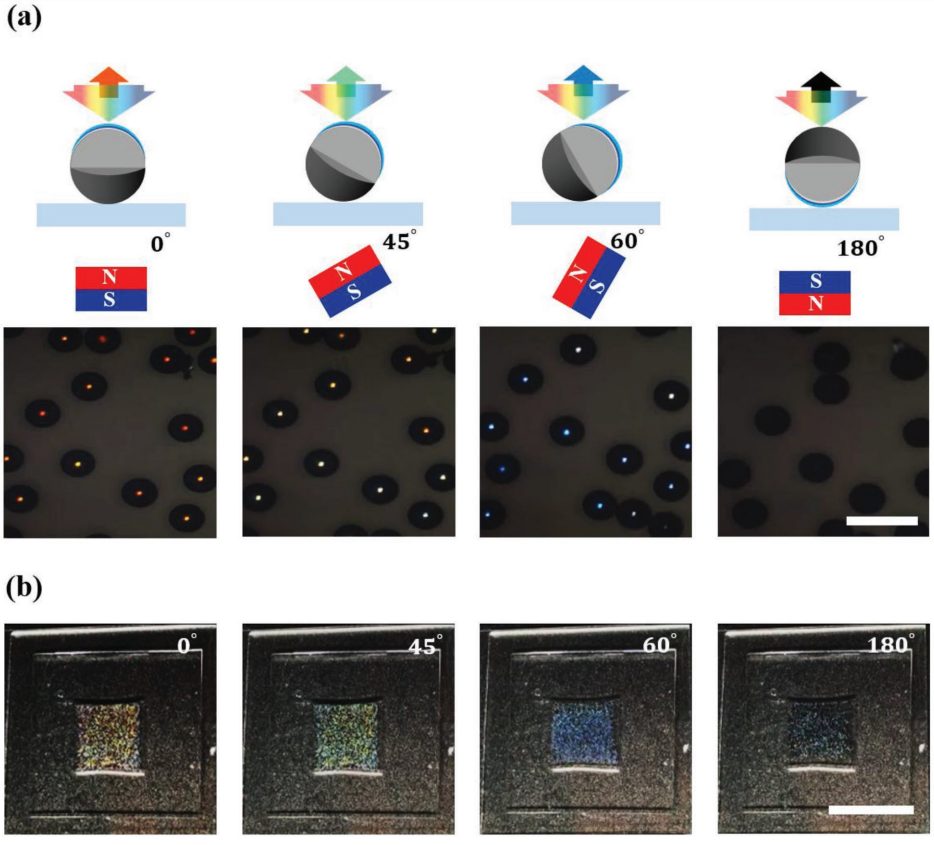

Figure 4. a) A series of schematics and OM images showing collective alignment and corresponding color of photonic Janus microspheres under external magnetic field with four different directions. The scale bar is 200 μm. b) A series of photographs showing the color change of microsphere array depending on the orientation of the microspheres. The scale bar is 1 cm.

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flux of the sputtering deposition results in a gradual variation of the thickness of photonic layers on each microsphere, thereby providing a structural color gradient. As the orientation of the microsphere is set by the direction of the external magnetic field, the structural color can be shifted or turned off on-demand. This tunability of structural color from a single particle is very difficult to achieve with photonic microspheres previously developed. As the formation of color gradient relies on the nature of directional deposition, spheres with various sizes can be used as long as the radius is much larger than the thickness of the deposited layer. The gradient can be altered when the thickness relative to the radius is larger than 0.1, as shown in Figure S10 (Supporting Information). We believe that the photonic Janus microspheres with a color gradient are potentially useful as active structural color pigments for outdoor signboards or wallpaper displays operated in reflection mode.

Experimental Section

Preparation of Uniform Microspheres: To prepare monodisperse black microspheres, capillary microfluidic devices composed of two tapered cylindrical capillaries were used that were coaxially assembled to have a tip-to-tip alignment in a square capillary. One of the tapered capillaries with an orifice diameter of 80 or 100 μm was used to inject ETPTA (M_n = 428 g mol^{-1}, Sigma-Aldrich) containing 2 wt%/wt% Sudan black B (Sigma-Aldrich) and 5 wt%/wt% Irgacure 2100 (Ciba Specialty Chemicals) at a volumetric flow rate of 100 μL h^{-1}. An aqueous solution of 7.5 wt%/wt% PVA (M_w = 13 000–23 000 g mol^{-1}, Sigma-Aldrich) was injected through the interstices between the tapered and square capillaries at 1500 μL h^{-1}. The drops were formed at the tip of the tapered capillary in a dripping mode, which flowed through the other tapered capillary with an orifice diameter of 200 μm. The drop formation and flow were observed using optical microscopy (Nikon, Eclipse TS100) equipped with a high-speed camera (Motion Scope M3). The drops were continuously exposed to UV light (Lichtzen Co., Innocure 100N,) while collecting them in a vial. Collected microspheres were washed several times with distilled water.

Deposition on Microspheres: To immobilize microspheres, 20 wt%/wt% PS (M_w = 35 000 g mol^{-1}, Sigma-Aldrich) in toluene was spin-coated on glass wafer at 3000 rpm and dried at room temperature for 10 min. This yielded 5 μm thick PS layer. Microspheres were loaded on the PS-coated wafer and annealed at 100 °C for 30 min. Iron was deposited on the substrate with thermal evaporation system (SCEN Tech Co., DC-200) at a deposition rate of 0.8 Å s^{-1} and a base pressure of 4 × 10^{-6} Torr. Chromium, silica, and titania were sputtered under a base pressure of 10^{-7} Torr, argon flow rate of 12 sccm, and radio frequency power of 150 W. The microspheres were released from PS-coated glass wafer by partially dissolving PS using toluene.

Characterization: Photonic Janus microspheres were observed using optical microscopy in reflection mode (Nikon, Eclipse L150) and scanning electron microscopy (SEM, Hitachi, S-4800); a focused ion beam was used for the observation of layer cross-section with SEM. The reflection spectra were measured using a fiber-coupled spectrometer (Ocean Optics Inc., USB 4000) equipped in the optical microscope, where 20× objective lens with numerical aperture of 0.45 was used. To make CIE chromaticity diagrams, *x*- and *y*-coordinates were obtained by reflectance spectra. The magnetization of the iron film was characterized with a vibrating sample magnetometer (Lake Shore, US/7407).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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[1] A. Walther, A. H. E. Müller, *Chem. Rev.* **2013**, *113*, 5194.
[2] F. Sciortino, A. Giacometti, G. Pastore, *Phys. Rev. Lett.* **2009**, *103*, 237801.
[3] F. Wurm, A. F. M. Kilbinger, *Angew. Chem., Int. Ed.* **2009**, *48*, 8412.
[4] L. Hong, S. Jiang, S. Granick, *Langmuir* **2006**, *22*, 9495.
[5] K.-H. Roh, D. C. Martin, J. Lahann, *Nat. Mater.* **2005**, *4*, 759.
[6] K. P. Yuet, D. K. Hwang, R. Haghgooie, P. S. Dole, *Langmuir* **2010**, *26*, 4281.
[7] J. Hu, S. Zhou, Y. Sun, X. Fang, L. Wu, *Chem. Soc. Rev.* **2012**, *41*, 4356.
[8] M. Yoshida, K.-H. Roh, S. Mandal, S. Bhaskar, D. Lim, H. Nandivada, X. Deng, J. Lahann, *Adv. Mater.* **2009**, *21*, 4920.
[9] J. N. Anker, R. Kopelman, *Appl. Phys. Lett.* **2003**, *82*, 1102.
[10] A. Walther, M. Hoffmann, A. H. E. Müller, *Angew. Chem., Int. Ed.* **2008**, *47*, 711.
[11] F. Tu, B. J. Park, D. Lee, *Langmuir* **2013**, *29*, 12679.
[12] B. P. Binks, P. D. I. Fletcher, *Langmuir* **2001**, *17*, 4708.
[13] N. Glaser, D. J. Adans, A. Boker, G. Krausch, *Langmuir* **2006**, *22*, 5227.
[14] T. Tanaka, M. Okayama, H. Minami, M. Okubo, *Langmuir* **2010**, *26*, 11732.
[15] N. G. Min, M. Ku, J. Yang, S.-H. Kim, *Chem. Mater.* **2016**, *28*, 1430.
[16] F. Wang, G. M. Pauletti, J. Wang, J. Zhang, R. C. Ewing, Y. Wang, D. Shi, *Adv. Mater.* **2013**, *25*, 3485.
[17] M. Marquis, D. Renard, B. Cathala, *Biomacromolecules* **2012**, *13*, 1197.
[18] N. K. Sheridon, E. A. Richley, J. C. Mikkelsen, D. Tsuda, J. M. Crowley, K. A. Oraha, M. E. Howard, M. A. Rodkin, R. Swidler, R. Sprague, *J. Soc. Inf. Disp.* **1999**, *7*, 141.
[19] T. Nisisako, T. Torii, T. Takahashi, Y. Takizawa, *Adv. Mater.* **2006**, *18*, 1152.
[20] Z. Nie, W. Li, M. Seo, S. Xu, E. Kumacheva, *J. Am. Chem. Soc.* **2006**, *128*, 9408.
[21] L. Shang, F. Shangguan, Y. Cheng, J. Lu, Z. Xie, Y. Zhao, Z. Gu, *Nanoscale* **2013**, *5*, 9553.
[22] N. G. Min, T. M. Choi, S.-H. Kim, *Macromol. Chem. Phys.* **2016**, DOI: 10.1002/macp.201600265.
[23] H. Fudouzi, Y. Xia, *Langmuir* **2003**, *19*, 9653.
[24] I. Lee, D. Kim, J. Kal, H. Baek, D. Kwak, D. Go, E. Kim, C. Kang, J. Chung, Y. Jang, S. Ji, J. Joo, Y. Kang, *Adv. Mater.* **2010**, *22*, 4973.
[25] H. S. Kim, T. S. Shim, H. Hwang, S.-M. Yang, S.-H. Kim, *Chem. Mater.* **2013**, *25*, 2684.
[26] Y. Hu, J. Wang, C. Li, Q. Wang, H. Wang, J. Zhu, Y. Yang, *Langmuir* **2013**, *29*, 15529.
[27] L. Shang, F. Shanqquan, Y. Cheng, J. Lu, Z. Xie, Y. Zhao, Z. Gu, *Nanoscale* **2013**, *5*, 9553.
[28] A. C. Arsenault, D. P. Puzzo, I. Manners, G. A. Ozin, *Nat. Photonics* **2007**, *1*, 468.

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[29] S.-H. Kim, S.-J. Jeon, W. C. Jeong, H. S. Park, S.-M. Yang, *Adv. Mater.* **2008**, *20*, 4129.
[30] Z. Yu, C.-F. Wang, L. Ling, L. Chen, S. Chen, *Angew. Chem., Int. Ed.* **2012**, *51*, 2375.
[31] S.-S. Liu, C.-F. Wang, X.-Q. Wang, J. Zhang, Y. Tian, S.-N. Yin, S. Chen, *J. Mater. Chem. C* **2014**, *2*, 9431.
[32] S.-Na. Yin, S. Yang, C.-F. Wang, S. Chen, *J. Am. Chem. Soc.* **2016**, *138*, 566.
[33] C. Negri, A. L. Sellerio, S. Zapperi, M. C. Miguel, *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 14549.
[34] Y. Zhao, H. Gu, Z. Xie, H. C. Shum, B. Wang, Z. Gu, *J. Am. Chem. Soc.* **2013**, *135*, 54.
[35] K. Chung, S. Yu, C.-J. Heo, J. W. Shim, S.-M. Yang, M. G. Han, H.-S. Lee, Y. Jin, S. Y. Lee, N. Park, J. H. Shin, *Adv. Mater.* **2012**, *24*, 2375.
[36] L. González-García, G. Lozano, A. Barranco, H. Míguez, A. R. González-Elipe, *J. Mater. Chem.* **2010**, *20*, 6408.
[37] J. Noh, H.-L. Liang, I. Drevensek-Olenik, J. P. F. Largerwall, *J. Mater. Chem. C* **2014**, *2*, 806.
[38] S. S. Lee, S. K. Kim, J. C. Won, Y. H. Kim, S.-H. Kim, *Angew. Chem., Int. Ed.* **2015**, *54*, 15266.
[39] B. E. A. Saleh, *Fundamentals of Photonics*, 2nd ed., Wiley, New York, USA **2007**.
[40] K.-T. Lee, C. Ji, D. Banerjee, L. J. Guo, *Laser Photonics Rev.* **2015**, *9*, 354.

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